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# Formation of secondary aerosols from gasoline vehicle exhausts when mixing with SO<sub>2</sub>

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## Abstract

SOA.

Sulfur dioxide (SO<sub>2</sub>) can enhance the formation of secondary aerosols from biogenic volatile organic compounds (VOCs), but its influence on secondary aerosol formation from anthropogenic VOCs, particularly complex mixtures like vehicle exhausts, is still poorly understood. Here we directly co-introduced gasoline vehicles exhausts (GVE) and SO<sub>2</sub>, a typical pollutant from coal burning, into a smog chamber to investigate the formation of secondary organic aerosols (SOA) and sulfate aerosols through photooxidation. In the presence of high concentration of SO<sub>2</sub>, new particle formation was enhanced while substantial sulfate was formed through the oxidation of SO<sub>2</sub>. The homogenous oxidation by OH radicals contributed a negligible fraction to the conversion 10 of SO<sub>2</sub> to sulfate, and instead the oxidation by stabilized Criegee intermediates (sCIs), formed from alkenes in the exhaust reacting with ozone, dominated the conversion of SO<sub>2</sub>. After 5 h of photochemical aging, GVE's SOA production factor revealed an increase by 60-200% in the presence of high concentration of SO<sub>2</sub>. This increase could largely be attributed to acid-catalyzed SOA formation, which was evidenced by 15 the strong positive linear correlation ( $R^2 = 0.97$ ) between the SOA production factor and in-situ particle acidity calculated by AIM-II model. A high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS) resolved OA's relatively lower oxygen-tocarbon (O:C) and higher hydrogen-to-carbon (H:C) molar ratios for the GVE/SO<sub>2</sub> mixture, with a much lower estimated average carbon oxidation state (OS<sub>c</sub>) of  $-0.51 \pm 0.06$ 20 than that of  $-0.19 \pm 0.08$  for GVE alone. The relative higher mass loading of OA in the experiments with SO<sub>2</sub> might be the major reason for the lower oxidation degree of



## 1 Introduction

As main components of fine particles or PM<sub>2.5</sub>, sulfate and organic aerosols (OA) can lead to serious and complex air pollution (Parrish and Zhu, 2009) and have negative effects on human health (Nel, 2005). Furthermore, sulfate and OA affect radiative forcing on global scale (Andreae et al., 2005; Shindell et al., 2009). A detailed understanding of the magnitude and formation pathways of sulfate and OA is therefore critical to formulate control strategies and accurately estimate their impact on air quality and climate, yet this attempt is often complicated due to the missing or underestimated oxidation pathways of sulfur dioxide (SO<sub>2</sub>) (Berglen et al., 2004), which is the precursor of sulfate, and the unclear formation mechanisms of secondary organic aerosols (SOA) (de Gouw et al., 2005; Heald et al., 2005; Johnson et al., 2006; Volkamer et al., 2006), which account for a large fraction of OA (Zhang et al., 2007).

SO<sub>2</sub>, mainly emitted from coal-fired power plants and coal-burning boilers, when mixed with gasoline vehicle exhausts containing a plenty of NO<sub>x</sub> and aromatics that provide precursors for the formation of secondary nitrates and organic aerosols, might react with each other and make the formation of sulfate and SOA complicated. The alkenes present in gasoline vehicle exhausts can react with ozone to form stabilized Criegee intermediates (CIs), which were recently considered to significantly oxidize SO<sub>2</sub> and thus influence the formation of sulfate (Mauldin et al., 2012; Welz et al.,

- 20 2012). On the other hand, recent smog chamber simulations indicated that SO<sub>2</sub> could enhance the SOA formation from typical biogenic precursors, such as monoterpenes and isoprene through acid-catalyzed reactions (Edney et al., 2005; Kleindienst et al., 2006; Jaoui et al., 2008), but the influence of acid-catalyzed reactions on SOA formation from aromatics is still debatable (Cao and Jang, 2007; Ng et al., 2007). In addition,
- these combinations of several pure chemicals could not well represent the mixing of SO<sub>2</sub> with vehicle exhausts brimming with thousands of gaseous and particle-phase components (Gordon et al., 2014) in the formation of secondary aerosols under real



atmospheric conditions. Till present no reports are available about the influence of  $SO_2$  on the formation of secondary aerosols from complex vehicle exhausts.

Here we directly introduced pipe exhausts from light-duty gasoline vehicles (LDGV) and  $SO_2$  into a smog chamber with a 30 m<sup>3</sup> Teflon reactor (Wang et al., 2014), to study the production of secondary aerosols: the influence of LDGV exhausts on the oxidation of  $SO_2$  to form sulfate aerosols and reciprocally that of  $SO_2$  on the formation of SOA from primary organics in LDGV exhausts.

# 2 Materials and methods

# 2.1 Vehicles and fuel

<sup>10</sup> Three LDGVs were used in this study, one Euro 1 and two Euro 4 vehicles. They are all port fuel injected vehicles with model years ranging from 2002 to 2011. More details of the individual vehicles are listed in Table 1. All the vehicles were fueled with Grade 93# gasoline, which complies with the Euro III gasoline fuel standard. Details of the gasoline composition can be found elsewhere (Zhang et al., 2013).

## 15 2.2 Smog chamber experiments

Six photochemical experiments of LDGV exhaust were conducted in a 30 m<sup>3</sup> indoor smog chamber in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). The details of the smog chamber were described by Wang et al. (2014). Briefly, black lamps (1.2 m-long, 60 W Philips/10R BL, Royal Dutch Philips Electronics Ltd, the Netherlands) are used as light source, providing a NO<sub>2</sub> photolysis rate of 0.49 min<sup>-1</sup>. Two Teflon-coated fans are installed inside the reactor to guarantee well mixing of the introduced gas species and particles within 120 s. In this study the temperature and relative humidity in the reactor were controlled at around 25 °C and 50 %, respectively. Before the introduction of vehicle exhaust, the vehicles were running on-



road for at least half an hour to warm up the three-way catalysts, and then the idling vehicle exhaust was introduced directly by two oil-free pumps (Gast Manufacturing, Inc, USA) into the reactor at a flow rate of  $40 L \text{min}^{-1}$ . Losses of volatile organic compounds (VOCs) and particles in the transfer lines were estimated to be less than 5% (Liu et al.,

<sup>5</sup> 2015). Prior to each experiment, the chamber was evacuated and filled with purified dry air for at least 5 times, then the reactor was flushed with purified dry air for at least 48 h until no residual hydrocarbons,  $O_3$ ,  $NO_x$ , or particles were detected in the reactor. The exhaust in the reactor was diluted by a factor of 13–94 compared to the tailpipe.

After the introduction of exhaust, SO<sub>2</sub> was injected by a gas-tight syringe to make

- <sup>10</sup> the mixing ratio of SO<sub>2</sub> in the reactor around 150 ppb during three experiments using the three vehicles. For comparison, experiments without additional SO<sub>2</sub> were also conducted for each vehicle. Additional NO was added to adjust the VOC / NO<sub>x</sub> ratios to between 4.9 and 10.8 (Table 2). VOC / NO<sub>x</sub> ratios in experiments with the same vehicle were similar. Initial concentrations of NO<sub>x</sub> ranged from 300.8 to 458.5 ppb. After <sup>15</sup> more than half an hour of primary characterization, the exhaust was exposed to black light continuously for 5 h. After the black lamps were switched off, the formed SOA was
- characterized for another 2 to 3 h to correct the particles wall loss. In this study, no OH precursor and seed particles were introduced.

An array of instruments was used to characterize gas and particle phase compounds in the reactor. Gas phase  $NO_x$ ,  $O_3$  and  $SO_2$  were measured with dedicated monitors (EC9810, 9841T, Ecotech, Australia, and Thermo Scientific Model 43iTLE, USA). The detection limit and accuracy of the  $SO_2$  instrument are 0.2 ppb and ±1 %, respectively. Methane and CO concentrations were determined using a gas chromatography (Agilent 6980GC, USA) with a flame ionization detector and a packed column (5A Molecular

Sieve 60/80 mesh, 3 m × 1/8 inch) (Zhang et al., 2012). CO<sub>2</sub> was analyzed with a HP 4890D gas chromatography (Yi et al., 2007). Gas phase organic species were measured with a Mode 7100 preconcentrator (Entech Instruments Inc., USA) coupled with an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector/electron capture detector (GC-MSD/FID, Agilent Technologies, USA) (Wang and Compared with a magine to the selection of the selector (GC-MSD/FID, Agilent Technologies, USA) (Wang and Compared with the selector (GC-MSD/FID, Agilent Technologies, USA) (Wang and Compared with the selector of the selector (GC-MSD/FID, Agilent Technologies, USA) (Wang and Compared with the selector of the selector (GC-MSD/FID, Agilent Technologies, USA) (Wang and Compared with the selector of the



Wu, 2008; Zhang et al., 2010, 2012, 2013) and a commercial proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS, Model 2000, Ionicon Analytik GmbH, Austria) (Lindinger et al., 1998; Jordan et al., 2009).  $C_2$ – $C_3$  and  $C_4$ – $C_{12}$  hydrocarbons were measured by GC-FID and GC-MSD, respectively. PTR-TOF-MS was used to determine the time-resolved concentrations of VOCs such as aromatics. The decay curve of toluene was used to derive the average hydroxyl radical (OH) concentration during

Particle number concentrations and size distributions were measured with a scanning mobility particle sizer (SMPS, TSI Incorporated, USA, classifier model 3080, CPC

- <sup>10</sup> model 3775). An aerosol density of 1.4 g cm<sup>-3</sup> was assumed to convert the particle volume concentration into the mass concentration (Zhang et al., 2005). A high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-MS, Aerodyne Research Incorporated, USA) was used to measure the particle chemical compositions and nonrefractory PM mass (Jayne et al., 2000; DeCarlo et al., 2006). The instrument was operated in the
- <sup>15</sup> high sensitivity V-mode and high resolution W-mode alternatively every two minutes. The toolkit Squirrel 1.51H was used to obtain time series of various mass components (sulfate, nitrate, ammonium and organics). We used the toolkit Pika 1.1H to determine the average element ratios of organics, like H:C, O:C, and N:C (Aiken et al., 2007, 2008). The contribution of gas-phase CO<sub>2</sub> to the m/z 44 signal was corrected using the measured CO<sub>2</sub> concentrations. The HR-TOF-MS was calibrated using 300 nm
  - monodisperse ammonium nitrate particles.

each experiment.

A summary of initial experimental conditions and final results is presented in Tables 2 and 3, respectively. Total wall-loss corrected OA varied from 17.8 to 91.4  $\mu$ g m<sup>-3</sup>, which span the typical urban PM concentrations in those heavy polluted megacities with poor <sup>25</sup> air quality. Primary OA (POA) concentrations of the experiments ranged from 0.13 to 0.31  $\mu$ g m<sup>-3</sup>, which are negligible compared with the formed SOA. Initial mixing ratios of non-methane hydrocarbons (NMHCs) in the reactor were between 2.2 and 4.3 ppm, much higher than typical urban conditions. Though initial NMHCs, NO<sub>x</sub> and average OH concentrations are different from typical urban conditions, we tried to maintain the



initial concentrations of the reactants as similar as possible for the same vehicle, so that all the changes in the SOA mass could be attributed to the effects of SO<sub>2</sub>.

# 2.3 SOA production factors

SOA production factor (PF)  $(mg kg^{-1})$  is calculated on a fuel basis:

$${}_{5} \text{ PF} = 10^{6} \times [\text{SOA}] \times \left( \frac{[\Delta \text{CO}_{2}]}{\text{MW}_{\text{CO}_{2}}} + \frac{[\Delta \text{CO}]}{\text{MW}_{\text{CO}}} + \frac{[\Delta \text{HC}]}{\text{MW}_{\text{HC}}} \right)^{-1} \times \frac{\omega_{\text{C}}}{\text{MW}_{\text{C}}}$$
(1)

where  $[\Delta CO_2]$ ,  $[\Delta CO]$ , and  $[\Delta HC]$  are the background corrected concentrations of  $CO_2$ , CO and the total hydrocarbons in the reactor in  $\mu g m^{-3}$ ; [SOA] is the concentration of wall-loss corrected SOA in  $\mu g m^{-3}$ ; MW<sub>CO2</sub>, MW<sub>CO</sub>, MW<sub>HC</sub>, and MW<sub>C</sub> are the molecular weights of CO<sub>2</sub>, CO, HC and C.  $\omega_C$  (0.85) is the carbon intensity of the gasoline (Kirchstetter et al., 1999). The total hydrocarbons measured in this study include methane and C<sub>2</sub>–C<sub>12</sub> hydrocarbons.

## 2.4 Determination of OH concentration

Decay of toluene measured by PTR-TOF-MS is used to determine the average OH concentration during each experiment. Changes in the toluene concentration over time can be expressed as:

$$\frac{d[\text{toluene}]}{dt} = -k \times [\text{OH}] \times [\text{toluene}]$$

where k is the rate constant for the reaction between toluene and OH radical. Assuming a constant OH concentration during an experiment, we can integrate Eq. (2) to get Eq. (3):

<sup>20</sup> 
$$\ln\left(\frac{[\text{toluene}]_0}{[\text{toluene}]_t}\right) = k \times [\text{OH}] \times t$$

15

(2)

(3)

So by plotting  $\ln([toluene]_0/[toluene]_t)$  vs. time *t*, we can obtain a slope that equals  $k \times [OH]$ . The average OH concentration is therefore calculated as:

 $[OH] = \frac{\text{slope}}{k}$ 

# 2.5 Determination of the steady state concentration of stabilized CIs

<sup>5</sup> The production of stabilized CIs in the atmosphere is dominated by ozonolysis of alkenes (Heard et al., 2004).

alkene +  $O_3 \longrightarrow Cls + products$ 

The four main losses of CIs are reactions with  $\rm H_2O,\,SO_2$  and  $\rm NO_2$  and unimolecular decomposition.

10

20

$CIs + H_2O \longrightarrow products$
$CIs + SO_2 \longrightarrow SO_3 + products$
$CIs + NO_2 \longrightarrow products$
$Cls \rightarrow products$

The steady state concentration of CIs will be

<sup>15</sup>  $CIs_{steady-state} = \frac{\phi K_{R1}[O_3][alkene]}{K_{R2}[H_2O] + K_{R3}[SO_2] + K_{R4}[NO_2] + K_{R5}}$ 

In this study, we estimated the steady state concentration of stabilized CIs throughout the whole experiment. The production rate of stabilized CIs depended on both the concentrations and composition of alkenes in the exhausts. Detailed gas-phase mechanisms of alkenes from the Master Chemical Mechanism version 3.3 or MCM v3.3 (http://www.chem.leeds.ac.uk/MCM) were run to determine the time-resolved concentrations of stabilized CIs in the experiments. Only the gas-phase mechanisms of

Discussion Paper ACPD 15, 23613-23649, 2015 **Formation of** secondary aerosols from gasoline vehicle Discussion **exhausts** T. Liu et al. Paper **Title Page** Abstract Introduction Discussion Paper Conclusions References Tables **Figures** < Back Close Discussion Paper Full Screen / Esc **Printer-friendly Version** Interactive Discussion

(4)

(R1)

(R2)

(R3)

(R4)

(R5)

(5)

alkenes were included in the model, with the concentrations of OH radicals, SO<sub>2</sub>, O<sub>3</sub> and NO<sub>2</sub> constrained to the measured concentrations.  $K_{R2}$ ,  $K_{R3}$ ,  $K_{R4}$  and  $K_{R5}$  for CH<sub>2</sub>OO, CH<sub>3</sub>CHOO, and (CH<sub>3</sub>)<sub>2</sub>COO used in the model were listed in Table 4. The rate coefficients for other stabilized CIs reacted with H<sub>2</sub>O, SO<sub>2</sub>, NO<sub>2</sub> and their uni-<sup>5</sup> molecular decomposition were assumed to be same as CH<sub>2</sub>OO. The yields of CH<sub>2</sub>OO, CH<sub>3</sub>CHOO, and (CH<sub>3</sub>)<sub>2</sub>COO used in the model were 0.37, 0.38 and 0.28, respectively. Yields of other stabilized CIs were assumed to be same as CH<sub>2</sub>OO.

## 2.6 Wall loss corrections

The loss of particles and organic vapors onto the reactor walls has to be accounted for to accurately quantify the SOA production. A detailed discussion of these corrections can be found elsewhere (Liu et al., 2015). The loss of particles onto the walls was treated as a first-order process (McMurry and Grosjean, 1985). The wall-loss rate constant was determined separately for each experiment by fitting the SMPS and AMS data with first-order kinetics when UV lamps were switched off. By applying this rate to

- the entire experiment, we use the same method as Pathak et al. (2007) to correct the wall loss of the particles. The wall loss of particles is a size-dependent process, therefore, the presence of nucleation would influence the wall loss correction of particles due to the rapid loss of nucleation mode particles. As shown in previous study, particle wall loss rates could not be accurately quantified for the particles generated in the nu-
- cleation event (Keywood et al., 2004). In this study, the impact of the nucleation event on wall-loss estimate is considered to be negligible for only less than 5 % of the particle mass is in the nucleation mode twenty minutes after nucleation for all the experiments. Wall deposition of organic vapors can lead to the underestimation of SOA production

(Matsunaga and Ziemann, 2010; X. Zhang et al., 2014, 2015). It is recently established that wall deposition of a compound is related with its volatility (Zhang et al., 2015).

The extent that wall deposition of organic vapors impacts on SOA production depends on the competition of organic vapors depositing onto walls and suspended particles. Here, we assumed that gas-particle partitioning of organic vapors dominated their wall



depositions and thus organic vapors were considered to only partition onto suspended particles.

As the collection efficiency of sulfate in the HR-TOF-AMS can vary due to the coating of OA onto sulfate, we used AMS data combined with SMPS data to derive the time-resolved concentrations of OA, sulfate, ammonium and nitrate. The ratio of OA to inorganic aerosols from the AMS was used to split the total particle mass measured by SMPS into the mass of OA, sulfate, ammonium and nitrate (Gordon et al., 2014; Liu et al., 2015).

### 3 Results and discussion

## 10 3.1 Formation of sulfate

Figure 1 shows the temporal evolution of gas- and particle-phase species during the photochemical aging of emissions from vehicle III with and without adding SO<sub>2</sub>. NO was injected to adjust the VOC / NO<sub>x</sub> ratio at approximately time = -0.25 h for both experiments. After the black lamps were turned on, NO was fast oxidized in less than 15 1 h. With or without SO<sub>2</sub>, mass concentrations of secondary aerosols started to climb rapidly after photooxidation for about 1 h, and became stabilized after about 4 h photooxidation (Figs. 1, 2 and 3). For experiments with SO<sub>2</sub>, substantial sulfate was formed synchronously with OA. The maximum particle number concentrations with SO<sub>2</sub> were 5.4–48 times of those without SO<sub>2</sub>. As the precursor of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), SO<sub>2</sub> at higher concentrations would lead to more H<sub>2</sub>SO<sub>4</sub> formed, and thereby increase the nucleation rates and total particle number concentrations (Sipila et al., 2010).

The formation rates of sulfate, derived from the differential of concentration-time plots of sulfate, exhibited burst increases at the initial stage of sulfate formation and then decreased to near zero 5 h after sulfate formation started (Fig. 5a). The maximum formation rate of sulfate in experiments I-2, II-2 and III-2 was 61.5, 21.6 and



113 μg m<sup>-3</sup> h<sup>-1</sup>, respectively, extremely higher than the rate of 0.17–0.37 ppbv h<sup>-1</sup> (0.73–1.59 μg m<sup>-3</sup> h<sup>-1</sup> under NTP condition) through gas-phase oxidation of SO<sub>2</sub> during the daytime in the Pearl River Delta (PRD) region of China in the summer of 2006 (Xiao et al., 2009), and also more than ten times higher than the maximum sulfate formation rate of 4.79 μg m<sup>-3</sup> h<sup>-1</sup> observed at an urban site in Beijing during the Beijing Olympic Games in 2008.

Normally, SO<sub>2</sub> was deemed to be oxidized by OH radicals through homogeneous reactions in gas-phase (Calvert et al., 1978), or by H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> through in-cloud processes in aqueous-phase (Lelieveld and Heintzenberg, 1992) that, however, could be negligible in this study because of RH around 50%. As shown in Fig. 6, the loss rate of SO<sub>2</sub> through homogeneous reactions with OH radicals in the three experiments ranged from 0.0023 to 0.0034 h<sup>-1</sup>, only accounting for 2.4–4.6% of the total loss rate of SO<sub>2</sub>. The initial concentrations of alkenes in the experiments with SO<sub>2</sub> varied from 248 to 547 ppb, contributing 7.7–23.5% of the total NMHCs. This high content of alkenes in the exhausts might form a mass of stabilized CIs through the reaction with ozone. Recent studies indicated that the rate coefficient of CH<sub>2</sub>OO with SO<sub>2</sub> was 50 to 10000 times larger than that used in tropospheric models (Welz et al., 2012). The oxidation of SO<sub>2</sub> by stabilized CIs could be as important as that by OH radicals in the atmosphere. Here, we estimated the steady state concentrations of

- <sup>20</sup> stabilized CIs throughout the whole experiments by running detailed gas-phase mechanisms of alkenes from the MCM v3.3. For experiments I-2 and III-2, the oxidation rate of SO<sub>2</sub> through the reactions with stabilized CIs was calculated to be  $0.071 \pm 0.033$  and  $0.045 \pm 0.022 h^{-1}$  (Fig. 6), respectively, accounting for 73.6 and 65.1 % of the total loss rate of SO<sub>2</sub>. Considering the variability of stabilized CIs throughout the whole experi-<sup>25</sup> ment, we concluded that stabilized CIs nearly took full responsibility for the oxidation of
- $SO_2$  in experiments I-2 and III-2. Whereas, the oxidation rate of  $SO_2$  through the reactions with stabilized CIs for the experiment II-2 was estimated to be  $0.030 \pm 0.017 h^{-1}$ , contributing 33.1 % of the total loss rate of  $SO_2$ . The unexplained loss of  $SO_2$  might be due to the heterogeneous oxidation in the presence of LDGV exhausts containing



massive aerosols and gaseous species. He et al. (2014) found that SO<sub>2</sub> could react with NO<sub>2</sub> on the surface of mineral dust to promote the conversion of SO<sub>2</sub> to sulfate. In this study, the reaction between SO<sub>2</sub> and NO<sub>2</sub> on the surface of existed aerosols might be a pathway to lead to the formation of sulfate.

### 5 3.2 SOA production

Fuel-based SOA production factors (PF), expressed as SOA production in milligram (mg) after 5 h photooxidation of LDGV exhausts emitted when per kilogram (kg) gasoline was burned, all increased substantially when adding SO<sub>2</sub>, 60-200% above that without SO<sub>2</sub> (Fig. 7a), although the selected cars' emission standards varied from Euro-I to Euro-IV. Accordingly when adding SO<sub>2</sub>, the in-situ particle acidities at the time when SOA formation rate peaks, calculated as H<sup>+</sup> concentrations based on AIM-II model  $H^+$ – $NH_4^+$ – $SO_4^{2-}$ – $NO_3$ – $H_2O$  with gas-aerosol partitioning disabled (http: //www.aim.env.uea.ac.uk/aim/model2/model2a.php) (Clegg et al., 1998; Wexler and Clegg, 2002), were 1.6–3.7 times as high as those without adding SO<sub>2</sub> (Table 3). This elevated particle acidity could largely explain the higher PFs of SOA from LDGV exhausts with SO<sub>2</sub>, supported by the strong positive linear correlations ( $R^2 = 0.965$ , P < 0.01) between SOA PFs and the in-situ particle acidities (Fig. 7b). Aromatic hydrocarbons are important SOA precursors in gasoline vehicle exhausts (Nordin et al., 2013; Gordon et al., 2014; Liu et al., 2015). The influence of particle acidity on SOA formation from aromatics is still debatable. Cao and Jang (2007) found that the pres-20 ence of acid seeds with [H<sup>+</sup>] concentrations of 240–860 nmol m<sup>-3</sup> greatly increased the SOA yields from oxidation of toluene and 1,3,5-trimethylbenzene as compared

with those using neutral seed aerosols. However, Ng et al. (2007) observed no influence of particle acidity on SOA yields from the aromatics, which might be due to the low content of aerosol water. In this study, SOA production from gasoline vehicle exhaust was enhanced even at a low level of [H<sup>+</sup>] concentrations ranging from 7.4 to 27.1 nmol m<sup>-3</sup>. Gas-phase oxidation products of aromatic hydrocarbons in the exhausts, like multifunctional carbonyl glyoxal, would be transformed more quickly to low



volatility products through acid-catalyzed heterogeneous reactions (Jang et al., 2002; Cao and Jang, 2007) and thus caused increasing SOA production. As shown in Fig. 8, the ion fragment m/z 88 that can only arise from a gloxyal oligomer (Liggio et al., 2005) had a higher intensity under higher acidity condition, indicating the important

<sup>5</sup> role of acid-catalyzed heterogeneous reactions in the SOA formation from gasoline vehicle exhaust. Recent studies indicated that the presence of high concentrations of seed aerosols might decrease the loss of organic vapors to the walls and thus increase the SOA formation (Kroll et al., 2007; X. Zhang et al., 2014, 2015). Therefore, the increase of condensation sinks due to the formation of sulfate with adding SO<sub>2</sub> might be another reason that caused the enhancement of SOA production.

SOA formation rates, derived from the differential of concentration-time plots of SOA, exhibited similar trends as sulfate with a burst increase at the initial stage of SOA formation (Fig. 5b). The average SOA formation rates for vehicles I, II and III with SO<sub>2</sub> were 1.1, 1.2 and 4.4 times as high as those without SO<sub>2</sub>, respectively, although the maximum rate for vehicle II with SO<sub>2</sub> was lower. Here we particularly focused on the burst increase stage of SOA and sulfate, which may be related to fast increase of PM<sub>2.5</sub> and occurrence of haze (He et al., 2014). Significant linear correlations (P < 0.05,  $R^2 > 0.88$ ) between SOA formation rate and particle acidity (Fig. 9) during this stage for experiments with SO<sub>2</sub> suggest that acid-catalyzed heterogeneous reactions might play an important role on the fast formation of SOA (Jang et al., 2002).

3.3 Oxidation state

After 5 h of photo-oxidation, SOA's molar ratios of oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) resolved by HR-TOF-AMS, were plotted on a Van Krevelen diagram (Heald et al., 2010) in Fig. 10. Relatively lower O:C and higher H:C for the <sup>25</sup> mixture of SO<sub>2</sub> and exhausts were observed than those for exhausts alone. The oxidation state of carbon (OS<sub>c</sub>), estimated from O:C and H:C, can be used to describe the chemistry and oxidative evolution of atmospheric organic aerosols (Kroll et al., 2011). Further calculated OS<sub>c</sub> revealed that averagely lower level of  $-0.51 \pm 0.06$  for SOA 23626



formed from LDGV exhausts with SO<sub>2</sub> when compared to that of  $-0.19 \pm 0.08$  without SO<sub>2</sub>, though they were all within or near the OS<sub>c</sub> range of -0.5-0 for semi-volatile OOA (SV-OOA) (Aiken et al., 2008). The relatively lower OS<sub>c</sub> with SO<sub>2</sub> indicated a lower oxidation degree of SOA. As Loza et al. (2012) did not observed a difference in

- <sup>5</sup> H: C and O: C for m-xylene SOA with neutral and acidic seed particles, acid-catalyzed heterogeneous reactions might not influence the oxidation degree of SOA in this study. Shilling et al. (2009) observed a lower O: C of SOA formed from the dark ozonolysis of  $\alpha$ -pinene at a higher mass loading of organic aerosols and suggested that the compounds partitioning into the particle phase at lower loadings were more oxygenated.
- <sup>10</sup> Kang et al. (2011) also observed that the oxidation degree of OA decreased rapidly as the OA mass concentration increased for the same amount of OH exposure. Given that the average OH concentrations were similar for the same vehicle (Table 2), the relative higher mass loading of OA in the experiments with SO<sub>2</sub> might lead to the lower O:C and thus decrease the oxidation degree of OA.

### 15 4 Conclusion

We reported a series of chamber experiments investigating the formation of secondary aerosols from the mixture of SO<sub>2</sub> and gasoline vehicle exhaust. The high content of alkenes in gasoline vehicle exhaust formed a plenty of stabilized CIs, which dominated the formation of sulfate. On the other hand, the elevated particle acidity due to the formation of sulfuric acid enhanced the SOA production from gasoline vehicle exhaust. We concluded that SO<sub>2</sub> and gasoline vehicle exhausts can enhance each other in forming secondary aerosols. Consequently, high concentration of SO<sub>2</sub> and high levels of aerosol acidity together with rapid increase of LDGVs in heavy polluted cities such as Beijing (Pathak et al., 2009; He et al., 2014) would make the air quality worse if there were no stricter control strategies on emissions of SO<sub>2</sub> and vehicle exhausts. Previous studies indicated that the high content of alkenes in China's gasoline oil was



Our results suggested that the incomplete combustion of gasoline with high content of alkenes might also induce the formation of stabilized CIs, which would facilitate the production of secondary aerosols. In China the limit of alkenes content was lowered to 24 % by volume in the newly established Level V gasoline fuel standard from 28 % by volume in the Level IV gasoline fuel standard. This limit is still quite higher when compared to those in USA or in Europe, and in particular, 6 times that in California, USA. Thus, limiting the content of alkenes in China's gasoline would benefit the control of both ozone and secondary aerosols.

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Table 1. Detailed	l information	of the th	ree LDGVs.
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ID	Emission standard class	Vehicle	Model year	Mileage (km)	Displacement (cm <sup>3</sup> )	Power (kW)	Weight (kg)
I	Euro4	Golf	2011	25000	1598	77	1295
Ш	Euro4	Sunny	2011	9448	1498	82	1069
	Euro1	Accord	2002	237984	2298	110	1423



Table 2. :	Summary of	the initial con	nditions durin	g the pho	otooxidatio	ו of LDG	V exhaus	ts.	aper   Discussi	Form seconda from gase exh T. Li	iatic ry a oline naus
Exp #*	$\begin{array}{c} \text{OH} (\times 10^6 \\ \text{molecules} \\ \text{cm}^{-3}) \end{array}$	7 (°C)	RH (%)	VOC / NO <sub>x</sub>	NMHCs (ppbv)	NO (ppbv)	NO <sub>2</sub> (ppbv)	SO <sub>2</sub> (ppbv)	ion Paper	Titl	e Paç
I-1	0.88	$25.0 \pm 0.8$	$52.9 \pm 2.0$	9.3	2896	300.6	9.5	8.6		Abstract	li
I-2	1.19	$25.5 \pm 0.3$	$53.6 \pm 2.5$	7.7	2323	281.4	19.5	151.8	_		
ll-1	1.29	$24.6 \pm 0.5$	$52.5 \pm 1.7$	10.8	4313	374	24.7	9	Ois	Conclusions	F
ll-2	1.08	$24.2 \pm 0.7$	$55.9 \pm 2.5$	9	3220	356	2.6	151.9	CU	Tablaa	
III-1	0.73	$24.1 \pm 0.6$	$57.0 \pm 2.0$	6	2582	431	0.6	9.2	SS.	Tables	
III-2	0.79	$24.3\pm0.3$	$57.9 \pm 1.2$	4.9	2243	454.6	3.9	154.1	on F		
Photooxid	ation experimen	ts of LDGV exh	austs named wit	h I, II and I	II refers to diff	erent vehic	les.		baper		



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Exp #	ΡΟΑ (μg m <sup>-3</sup> )	SOA (µg m <sup>-3</sup> )	Sulfate (µg m <sup>-3</sup> )	Ammonium (μg m <sup>-3</sup> )	Nitrate (µg m <sup>-3</sup> )	Particle number (cm <sup>-3</sup> ) <sup>a</sup>	[H <sup>+</sup> ] <sup>b</sup> (nmol m <sup>-3</sup> )
I-1	0.31	77.6	0.7	17.1	65.9	85182	12.5
I-2	0.21	91.2	67.5	17.6	6.1	563705	21.9
II-1	0.28	30.7	_	2.6	5.6	7427	10.4
II-2	0.13	37.3	38.1	9.7	1.9	357673	16.5
III-1	0.17	17.6	-	0.1	0.7	116143	7.4
III-2	0.23	77	76.7	19.2	5.3	630620	27.1

<sup>a</sup> Maximum particle number concentrations were without wall loss corrections.

<sup>b</sup> The concentration of H<sup>+</sup> in particle phase shown here was the value when the SOA formation rate reached the maximum during each experiment.



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**Table 4.** Summary of the final results during the photooxidation of LDGV exhausts.

Stabilized CIs	$10^{15} \text{ K}_{\text{R2}}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$10^{11} \text{ K}_{\text{R3}}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$10^{12} \text{ K}_{\text{R4}}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	K <sub>R5</sub> (s <sup>-1</sup> )
CH <sub>2</sub> OO	0.025 <sup>a</sup>	3.9 <sup>b</sup>	7.0 <sup>b</sup>	0 <sup>c</sup>
CH <sub>3</sub> CHOO	7.0 <sup>d</sup>	4.55 <sup>d</sup>	2.0 <sup>d</sup>	67.5 <sup>e</sup>
(CH <sub>3</sub> ) <sub>2</sub> COO	2.1 <sup>c</sup>	2.4 <sup>c</sup>	2.0 <sup>c</sup>	151 <sup>c</sup>

<sup>a</sup> Ouyang et al. (2013); <sup>b</sup> Welz et al. (2012); <sup>c</sup> Newland et al. (2015); <sup>d</sup> Taatjes et al. (2013); <sup>e</sup> Average of K<sub>R5</sub> from Fenske et al. (2000) and Newland et al. (2015).



**Figure 1.** Concentration–time plots of NO (left *y* axis) and particle–phase species (right *y* axis) during the photochemical aging of emissions from vehicle III. (a) Without SO<sub>2</sub>, and (b) with SO<sub>2</sub>. At time = 0 h, the black lamps were turned on.





**Figure 2.** Concentration–time plots of NO (left *y* axis) and particle–phase species (right *y* axis) during the photochemical aging of emissions from vehicle I. (a) Without SO<sub>2</sub>, and (b) with SO<sub>2</sub>. At time = 0 h, the black lamps were turned on.





**Figure 3.** Concentration–time plots of NO (left *y* axis) and particle–phase species (right *y* axis) during the photochemical aging of emissions from vehicle II. (a) Without SO<sub>2</sub>, and (b) with SO<sub>2</sub>. At time = 0 h, the black lamps were turned on.

















**Figure 6.** The oxidation rate of SO<sub>2</sub> during the photooxidation of LDGV exhausts with SO<sub>2</sub>. The loss rates of SO<sub>2</sub> reacting with OH radicals and stabilized CIs were calculated by multiplying the reaction rate coefficients derived from the MCM v3.3 by the average OH concentration and estimated stabilized CIs concentration, respectively. Error bars represent the standard derivation (1 $\sigma$ ) of the oxidation rate of SO<sub>2</sub> by stabilized CIs throughout the whole experiment.





**Figure 7.** SOA production factor (PF) and its relationship with particle acidity. **(a)** SOA PF after 5 h of photochemical aging of exhausts from different LDGVs with and without additional SO<sub>2</sub>. **(b)** SOA PF as a function of in-situ particle acidity. The concentration of  $H^+$  in particle phase shown here was the value when the SOA formation rate reached the maximum during each experiment.





Figure 8. Time evolution of m/z 88 during the aging of LDGV exhaust from vehicle III.











**Figure 10.** O: C vs. H: C of SOA formed from LDGV exhaust with and without additional SO<sub>2</sub> at the end of each experiment. Blue and red symbols represent data with and without additional SO<sub>2</sub>, respectively. The dashed lines represent estimated average carbon oxidation states of -1, -0.5, 0.5 and 1 (Kroll et al., 2011). The black lines represent the addition of functional groups to an aliphatic carbon (Heald et al., 2010).

